



## Estimations of historical atmospheric mercury concentrations from mercury refining and present-day soil concentrations of total mercury in Huancavelica, Peru

Nicholas A. Robins <sup>a,b,\*</sup>, Nicole Hagan <sup>b</sup>, Susan Halabi <sup>c</sup>, Heileen Hsu-Kim <sup>d</sup>, Ruben Dario Espinoza Gonzales <sup>e</sup>, Mark Morris <sup>f</sup>, George Woodall <sup>g</sup>, Daniel deB. Richter <sup>h</sup>, Paul Heine <sup>h</sup>, Tong Zhang <sup>d</sup>, Allan Bacon <sup>h</sup>, John Vandenberg <sup>g</sup>

<sup>a</sup> Department of History, North Carolina State University, 467 Withers Hall, Raleigh, NC 27695, USA

<sup>b</sup> Oak Ridge Institute for Science and Education, U.S. Environmental Protection Agency, 109 T.W. Alexander Drive, Research Triangle Park, NC 27711, USA

<sup>c</sup> Department of Biostatistics and Bioinformatics, Duke University, Box 2717 Medical Center, Durham, NC 27710, USA

<sup>d</sup> Department of Civil and Environmental Engineering, Duke University, Box 90287, Hudson Hall, Durham, NC 27708, USA

<sup>e</sup> Environmental Health Council, Jr. San Juan Evangelio 527, Ascension, Huancavelica, Peru

<sup>f</sup> Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, 109 T.W. Alexander Drive, Research Triangle Park, NC, USA

<sup>g</sup> Office of Research and Development, U.S. Environmental Protection Agency, 109 T.W. Alexander Drive, Research Triangle Park, NC, USA

<sup>h</sup> Nicholas School of the Environment, Duke University, Box 90328, LSRC, Durham, NC 27708, USA

### ARTICLE INFO

#### Article history:

Received 29 November 2011

Received in revised form 27 March 2012

Accepted 30 March 2012

Available online 26 April 2012

#### Keywords:

Mercury

Silver

AERMOD

Soils

Huancavelica, Peru

### ABSTRACT

Detailed Spanish records of cinnabar mining and mercury production during the colonial period in Huancavelica, Peru were examined to estimate historical health risks to the community from exposure to elemental mercury (Hg) vapor resulting from cinnabar refining operations. Between 1564 and 1810, nearly 17,000 metric tons of Hg were released to the atmosphere in Huancavelica from Hg production. AERMOD was used with estimated emissions and source characteristics to approximate historic atmospheric concentrations of mercury vapor. Modeled 1-hour and long-term concentrations were compared with present-day inhalation reference values for elemental Hg. Estimated 1-hour maximum concentrations for the entire community exceeded present-day occupational inhalation reference values, while some areas closest to the smelters exceeded present-day emergency response guideline levels. Estimated long-term maximum concentrations for the entire community exceeded the EPA Reference Concentration (RfC) by a factor of 30 to 100, with areas closest to the smelters exceeding the RfC by a factor of 300 to 1000. Based on the estimated historical concentrations of Hg vapor in the community, the study also measured the extent of present-day contamination throughout the community through soil sampling and analysis. Total Hg in soils sampled from 20 locations ranged from 1.75 to 698 mg/kg and three adobe brick samples ranging from 47.4 to 284 mg/kg, consistent with other sites of mercury mining and use. The results of the soil sampling indicate that the present-day population of Huancavelica is exposed to levels of mercury from legacy contamination which is currently among the highest worldwide, consequently placing them at potential risk of adverse health outcomes.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

### 1.1. Huancavelica, Peru

Colonial cinnabar mining began in Peru at the Santa Barbara Hill near Huancavelica in 1564. Colonial miners and refiners initially exported mercury to New Spain, present-day Mexico, where silver production through mercury amalgamation began in the 1550s

(Cooke et al., 2009; Robins, 2011). The introduction of the amalgamation system to the Andes in the 1570s was accompanied by the imposition of the *mita* system of forced, fixed term indigenous labor. The ranks of these forced workers declined steadily throughout the colonial era as a result of metal toxicity and flight from service which left the surrounding provinces largely depopulated (Robins, 2011).

Mercury refining involved the extraction and crushing of ore, and its subsequent smelting in which the mercury was volatilized, collected and ultimately shipped in liquid form to Andean silver mining centers, the most famous of which was Potosi in present-day Bolivia. Broken cinnabar ore was fired on a grate which stood approximately two to three meters off the ground in a conical roofed chamber to which it was connected to condensation tubes that passed through water on their way to a point of collection. After about four hours of combustion, draft laborers closed the air supply and were to allow the smelter to cool for about 24 h. They would then enter the

\* Corresponding author at: Department of History, North Carolina State University, Withers Hall 268, Raleigh, NC 27695-8108, USA. Tel.: +1 919 490 6937.

E-mail addresses: [narobins@ncsu.edu](mailto:narobins@ncsu.edu) (N.A. Robins), [hagan.nicole@epa.gov](mailto:hagan.nicole@epa.gov) (N. Hagan), [susan.halabi@duke.edu](mailto:susan.halabi@duke.edu) (S. Halabi), [hsukim@duke.edu](mailto:hsukim@duke.edu) (H. Hsu-Kim), [espinozai@hotmail.com](mailto:espinozai@hotmail.com) (R.D.E. Gonzales), [morris.mark@epa.gov](mailto:morris.mark@epa.gov) (M. Morris), [woodall.george@epa.gov](mailto:woodall.george@epa.gov) (G. Woodall), [drichter@duke.edu](mailto:drichter@duke.edu) (D. Richter), [pheine@duke.edu](mailto:pheine@duke.edu) (P. Heine), [tong.zhang@duke.edu](mailto:tong.zhang@duke.edu) (T. Zhang), [allan.bacon@duke.edu](mailto:allan.bacon@duke.edu) (A. Bacon), [vandenberg.john@epa.gov](mailto:vandenberg.john@epa.gov) (J. Vandenberg).

chamber to collect the mercury on the ceiling and in the ash which had not passed through the condensation system. Despite their utility, the smelters in Huancavelica were inefficient, and mercury vapor and liquid regularly escaped from the poorly sealed joints, which was exacerbated by overheating of the ovens (Robins, 2011).

Based on colonial records of production levels of mercury in Huancavelica, an estimated 17,000 metric tons of mercury vapor escaped the smelters between 1564 and 1810, which potentially deposited in the surrounding area (Robins and Hagan, 2012). An average of 69 metric tons of mercury per year was emitted to Huancavelica's atmosphere. As a comparison, Telmer and Viega (2008) estimated that 350 metric tons of mercury is emitted globally each year from artisanal and small scale gold refining.

### 1.2. Health effects from mercury exposure

While individual sensitivity to mercury exposure varies, mercury poisoning may limit immune response and increase vulnerability to allergies and infections (ATSDR, 1999). Chronic elemental mercury poisoning produces physical symptoms which include tremors, pallidity, gum discoloration, loose teeth, excessive salivation, gingivitis, anemia, difficulty speaking, lack of appetite, and loss of muscular control. Such symptoms are often in concert with clinical and subclinical neuropsychological effects which may be persistent and in some cases irreversible. These include personality changes, irascibility, impatience, hypercriticism, shyness, depression, anxiety, loss of memory, obsessive–compulsive disorders, and problems concentrating and making decisions (U.S. EPA, 1997).

### 1.3. Comparison of global soil mercury contamination

The extent of soil mercury contamination from mining activities has been well-documented (see Table 5). Locations such as Almadén, Spain and Idrija, Slovenia were the largest mercury mines in the world, and the legacy of contamination still remains a large concern even after mining has ceased. The Santa Barbara mine near Huancavelica was another major site for mercury mining, but the distinction of this area is that much of the ore processing occurred in Huancavelica, a town that is densely populated by residents who remain largely unaware of the levels of mercury in the soil of their community.

Native soil contains both organic and inorganic species of mercury resulting from anthropogenic and natural releases into the environment, coupled with microbial and chemical activity in the soil. Because of potential human health and environmental risks, mercury is typically regulated by many government agencies. Mercury can be speciated in soil, but elemental mercury is the primary target of government regulations and management activities. All species of mercury pose a health and environmental risk, with organic species of mercury posing a greater health risk than inorganic species (Revis et al., 1990).

To our knowledge, this is the first study of widespread historical and present-day mercury contamination within the city of Huancavelica, Peru. Through use of an air dispersion model, this study aims to estimate historical health risks to the community from exposure to elemental mercury vapor resulting from cinnabar refining operations during the colonial period. Based on the estimated historical concentrations of mercury vapor in the community, the study also measured the extent of present-day contamination throughout the community through soil sampling and analysis. The results of this study will serve as the foundation for future research efforts of human exposures to historical mercury contamination in the city, particularly residential exposure.

## 2. Methods

### 2.1. Emission data

Spanish records of mercury produced in Huancavelica in 1680, a year representative of high production, were evaluated. Mercury emission rates,  $E_m$ , (in grams per mill per second) were estimated from the mercury produced in Huancavelica and registered with the colonial government using Eq. (1) for mills within the city.

$$E_m = \frac{\left(\frac{Hg_{reported}}{1-c}\right)\left(\frac{1}{1-V_1}\right) \times V_2}{n \times t} \quad (1)$$

The total mass of reported mercury production,  $Hg_{reported}$ , for 1680 was 594 metric tons. Taking into account widespread unregistered production (or contraband,  $c$ , which is the fraction of the total mercury produced in the mills and not reported to the government, approximately 25%) in Huancavelica, we estimated that 792 metric tons of mercury was actually produced in the city in 1680. A range of contraband has been estimated to be from 10% to 66%, depending on the time period. A thorough review of the literature provides evidence of a more reasonable range of 25% to 30% for the percentage of contraband (Robins, 2011). A volatilization fraction,  $V_1$ , of 25% was used to account for the total amount of mercury vapor released from the refining of reported and contraband cinnabar. This results in the 1056 metric tons of cinnabar ore that was available for refining at the beginning of the process. A second volatilization fraction,  $V_2$ , of 25% was used to estimate the total amount of mercury vapor released from the refining of 1056 metric tons of cinnabar ore, which equals 264 metric tons of mercury vapor. This volatilization fraction ( $V_2$ ) is consistent with other values in the literature, including a recent study of 22 Chinese artisanal smelters that found a mean emission rate just under 20% (Li et al., 2008a). The total emissions were distributed equally among the number of mills in the city ( $n$ , 13 mills in 1680) and adjusted for units of time,  $t$ . This resulted in an emission rate,  $E_m$ , of 0.64 g of mercury per mill per second for 1680.

### 2.2. AERMOD

This study employed AERMOD, a plume dispersion and air quality model developed by the American Meteorological Society (AMS) and the United States Environmental Protection Agency (U.S. EPA). AERMOD predicts plume dispersion and ambient air concentrations at various distances from the source on the basis of source characteristics including meteorological conditions, emissions temperature, exit velocity and stack height and diameter (U.S. EPA, 2009a). AERMOD was used as a primary tool for a first approximation of the distribution of present-day soil contamination resulting from the release of mercury vapor during cinnabar refining.

AERMOD input data are usually derived from preprocessors AERMAP and AERMET. AERMAP provides geographical information, including elevation data. Although located in a mountainous region, the city of Huancavelica itself lies in a steep valley and the terrain of the valley floor is essentially flat. Considering the gentle slopes and low level emission releases, the terrain within the city is not expected to affect the concentrations; therefore, AERMAP was not utilized in this exercise. AERMET typically provides the meteorological data, which generally utilizes one to five years of hourly measured meteorological data to generate the files necessary to run AERMOD. Because long-term meteorological measurements were lacking for Huancavelica, AERMET was not used in this exercise. Instead, MAKEMET (U.S. EPA, 2010) was used to generate a matrix of meteorological conditions based on a minimum number of inputs, including ambient temperature range and land surface characteristics. AERMOD was used with MAKEMET meteorological data and the resulting air concentration estimates for the 1806 receptor

sites (50 m spacing) within Huancavelica are 1 hour (1-h) concentrations. The 1-h concentrations were extrapolated to long-term concentrations by applying a conversion factor of 0.08 (NRC, 1994).

AERMOD was run using flat terrain, rural dispersion, and all regulatory default options except by-pass date checking for non-sequential meteorological data file, which accounted for the use of MAKEMET meteorological data rather than Huancavelica-specific meteorological data, which is unavailable for the colonial period. Source characteristics were derived from archival documents and images (Hagan et al., 2011; Robins, 2011), as well as from firsthand assessments of smelter ruins.

### 2.3. Present-day soil mercury concentrations

Total mercury concentrations were measured in soil samples collected in the Huancavelica community. The AERMOD results suggest a distribution of modeled historical mercury air concentrations across the Huancavelica community, declining with distance from smelter sources. Sampling locations were selected based in part on the expertise of a local archaeologist and historical maps of the locations of the historical mill sites. In June 2009, soil samples were collected from fifteen sites located 350 m to 750 m apart to evaluate the extensive distribution of total mercury in present-day soils. At each site, three replicate samples were collected from the top 2.5 and 7.5 cm of soil within a 1-m<sup>2</sup> area. Adobe brick samples (X, Y, Z) were also taken from three homes in 2009 by scraping the sample from exposed exterior adobe brick. In August 2010, five additional sites (K, L, M, N, O) were sampled at a depth of 2.5 and 7.5 cm. Samples were taken from soil that either appeared undisturbed or from depths that would eliminate concern about soils that were not original to Huancavelica. Notes were taken regarding characteristics of each sample location, indicating any soil that may have been brought from another location and used as fill. All samples were stored in polypropylene centrifuge tubes in a sealed plastic container for transport. Samples were stored in the laboratory at 4 °C until analysis.

In the 2010 field survey, *in-situ* gaseous elemental mercury (Hg<sup>0</sup>) measurements were also collected at five sampling sites (K, L, M, N, O) using a handheld mercury vapor analyzer (Jerome J405, Arizona Instruments). Prior to sampling the soil, four consecutive mercury vapor measurements were collected at one m above the ground. Here we report the data as an average  $\pm$  1 standard deviation of the four measurements. The detection limit for this instrument is approximately 0.5  $\mu\text{g}/\text{m}^3$ ; thus, concentrations below this value were treated as zero in the averaging of data.

Total mercury concentrations in soil and adobe samples collected in 2009 were estimated by direct thermal decomposition, amalgamation, and atomic absorption spectrophotometry (Milestone DMA-80, EPA Method 7473; U.S. EPA, 1998). Instrument calibrations were performed with an acidified mercuric nitrate stock solution and verified with a NIST-certified standard reference material (2709 San Joaquin soil). The recovery of total mercury in the standard reference material (SRM) was 106%. Samples with concentrations greater than 125 mg/kg were first digested by hot plate extraction in 1:1 HCl:H<sub>2</sub>SO<sub>4</sub> for at least 1 h. After digestion, the extract was diluted in 0.5% bromine monochloride and analyzed by the DMA-80. Analysis of the NIST 2709 SRM by HCl-H<sub>2</sub>SO<sub>4</sub> acid digestion resulted in mercury recoveries that were 93% of certified mercury concentrations.

Total mercury concentrations in soil samples from the 2010 field survey were determined with a slightly different approach. Some of the 2009 soil samples were beyond the range of detection for the Milestone DMA-80 and required digestion prior to analyses. Through the acquisition of an automatic cold vapor atomic fluorescence spectrometry instrument after the analysis of the 2009 soil samples, it was possible to measure total mercury by the digestion method for all 2010 samples. The samples were first digested by hot block extraction in 4:1 HCl:HNO<sub>3</sub> at 85 °C for 5 h. After digestion, the extract was diluted in 0.5% bromine monochloride and then analyzed for mercury

content by stannous chloride reduction, gold amalgamation, cold vapor atomic fluorescence spectrometry (Brooks Rand MERX-T; EPA Method 1631; U.S. EPA, 2002). Instrument calibrations were performed with an acidified mercuric nitrate stock solution. The recovery of mercury from HCl-HNO<sub>3</sub> digested NIST 2709 was 120% of certified mercury concentrations. Recovery of mercury from the NIST 2709 SRM was within the acceptable range of the certified value for both analysis methods.

Subsamples of the soils were dried at 101 °C and weighed for determination of wet/dry weight ratio. All concentrations are reported on a dry weight basis and represent the average total mercury concentrations of triplicate samples collected at each location.

Two soil samples and two adobe samples were also analyzed for mercury speciation using a previously established sequential extraction technique (Bloom et al., 2003). In summary, the procedure involves stepwise extraction of mercury from a soil sample that is exposed to the following reagents (listed in sequential order): deionized water, 0.1 M acetic acid + 0.01 M HCl (pH 2), 1 M KOH, 12 M HNO<sub>3</sub>, and 10 mL HCl + 3 mL HNO<sub>3</sub>. The dissolution of mercury in a respective leaching solution provides empirical information regarding chemical reactivity of the mercury and information toward mercury speciation. Soils were mixed end-over-end for 18 h in each reagent. After mixing, the samples were centrifuged to separate the leachate from the sample. Leachates were decanted, filtered (0.4  $\mu\text{m}$ ), and preserved with 0.5% BrCl (v/v) until analysis for total mercury. The sum of mercury over the five extraction solutions relative to the total Hg content (quantified directly by HCl/H<sub>2</sub>SO<sub>4</sub> digestion) varied widely between the four samples (from 116% to 226%).

### 2.4. Soil characteristics

#### 2.4.1. Compositing samples

Due to limited sample mass, soils were composited for analysis of pH, carbon content, and texture. Huancavelica 2009 samples were composited by depth (0–2.5 cm and 2.5–7.5 cm) for each of five sampling locations along 3 transects to yield 15 samples for analysis. Where possible, 0.25 g from six field replicates collected at each transect point was combined to yield a 1.5 g composite sample. For the 2009 adobe samples, enough material was collected to measure three field replicates individually for pH and total carbon. The adobe field replicates were composited for texture analysis.

Huancavelica 2010 samples were of sufficient mass to measure pH and total carbon at 0–2.5 cm and 2.5–7.5 cm depths at each of the five points along the transect. For texture analysis, the depths were composited to yield five measurements along the transect.

#### 2.4.2. Sieving and grinding

All Huancavelica 2010 samples were air-dried and sieved (ASTM #10 sieve) prior to pH and texture analysis. All 2009 and 2010 samples were pulverized with an agate mortar and pestle prior to total carbon analysis.

#### 2.4.3. pH

Soil pH was measured in 0.01 M CaCl<sub>2</sub> using a 10:1 SSR on a Beckman Model 360 pH Meter (Beckman Instruments, Fullerton, CA) standardized on 4 and 10 buffers (Hendershot et al., 1993).

#### 2.4.4. Organic carbon

To estimate soil organic carbon, samples were analyzed for total carbon on a ThermoQuest Flash EA1112 Elemental Analyzer (ThermoQuest Italia, Milan, Italy) before and after dry-ashing at 550 °C for four hours in a Thermo Fisher Scientific Model F6020C Furnace (Thermo Fisher Scientific, Asheville, NC). Soil organic carbon was calculated as the difference in total carbon between ashed and unashed samples. Complete recovery of inorganic carbon was verified by measuring total carbon on ashed CaCO<sub>3</sub> (McGill and Figueiredo, 1993). A subset of samples were analyzed



**Table 1**

Inhalation reference values for elemental mercury vapor (adapted from U.S. EPA, 2009b).

Reference value type/name	Reference value (mg/m <sup>3</sup> )
Acute	
AEGL-3 (1-h)	8.9
AEGL-2 (1-h)	1.7
NIOSH Ceiling (10-min)	0.1
NIOSH REL (10-h TWA)	0.05
CalEPA REL (1-h)	0.0006
Chronic	
EPA RFC	0.0003

for total carbon in duplicate. Relative standard deviations ranged from 0.03% to 1.7%.

#### 2.4.5. Texture analysis

Percent sand, silt, and clay were estimated gravimetrically by the pipette method on 25 g composite samples using Calgon (Benckiser Consumer Products, Greenwich, CT) as the chemical dispersing agent and an ELE International stirrer (Soiltest Products Division, Lake Bluff, IL) for mechanical dispersion (Gee and Or, 2002). The measurements were performed only once per location (due to limited sample mass). However based on our previous experience with the instrumentation and soils of similar texture, we expect the relative

standard deviations to be approximately 10% of the clay fraction and 2% of the sand fraction.

### 3. Results

#### 3.1. Dispersion model estimates and health reference levels

Drawing from the relevant scientific literature, federal, state and professional organizations have developed reference values for inhalation exposure to elemental mercury vapor for the general public, as well as for occupational and emergency response settings (U.S. EPA, 2009b). These reference values reflect different durations of exposure, and generally include uncertainty factors to ensure that target populations, such as individuals with pre-existing conditions, children, or the elderly, are protected. This study utilizes the following acute inhalation reference values for comparison to short-term ambient concentration estimates: the California Environmental Protection Agency (CalEPA) Acute Reference Exposure Level (REL) for 1-h exposures, the National Institute for Occupational Safety and Health (NIOSH) Recommended Exposure Limit (REL) for 10-h exposures, the NIOSH Ceiling value for 10-min exposures, and the Acute Exposure Guideline Levels (AEGLs) for 1-h exposures. Long-term ambient air concentration estimates were compared to the U.S. EPA Reference Concentration (RFC).



**Fig. 1.** Estimated 1-h ambient air mercury concentrations for Huancavelica in 1680 and comparison with acute inhalation reference values.

AEGL values concern “once-in-a-lifetime” emergency response exposure scenarios for the general public. The AEGL-2 is a level above which irreversible health effects or limitations on the ability to escape may result, while exposures exceeding the AEGL-3 levels may be lethal (NRC, 2001). The NIOSH Ceiling value reflects a level that should never be exceeded during a 10-h work day in a 40-h work week (NIOSH, 2006). The CalEPA Acute (1-h) REL is “the concentration level at or below which no adverse health effects are anticipated for a specified exposure duration” and “are designed to protect the most sensitive individuals in the population by the inclusion of margins of safety” (OEHHA, 2008). The U.S. EPA RfC is a value for chronic exposure and “is an estimate (with uncertainty spanning perhaps an order of magnitude) of continuous inhalation exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime” (U.S. EPA, 1995a). Present-day inhalation reference values used in this study are shown in Table 1.

Mercury ambient air concentration estimates for 1680 were compared with present-day inhalation reference values for elemental mercury vapor to characterize historical risk potential. The entire community of Huancavelica was estimated to have experienced maximum 1-h concentrations of mercury that exceeded present-day inhalation reference values, as shown in Fig. 1. The entire community of Huancavelica was also estimated to have exceeded the NIOSH Ceiling value, while some of the areas closest to the mercury refining mills exceeded the AEGL-2 value.

Maximum long-term mercury concentrations were estimated by multiplying the 1-h estimated mercury concentrations by 0.08 (NRC, 1994) and compared with the EPA RfC, as shown in Fig. 2. The entire community was estimated to have exceeded the RfC by a factor of 30 to 100. Areas closer to the sources, within approximately 300 m of the mercury smelters, were estimated to have exceeded the RfC by a factor of 100 to 300. The areas closest to the smelters (within about 100 m) were estimated to have exceeded the RfC by a factor of 300 to 1000.

### 3.2. Present-day soil measurements

The AERMOD results suggested a distribution of steeply increasing atmospheric mercury concentrations with proximity to smelters. The geographic variability of mercury concentration in sampled soils (ranging from 1.75 to 698 mg/kg) generally followed a similar trend to the modeled distribution (Fig. 2). The average mercury concentration in soils from the reference site, Sucre, a non-mining city in Bolivia, was  $0.041 \pm 0.021$  mg/kg ( $n = 10$ ), 30 to 35,000 times lower than the concentrations in the soils of Huancavelica. The locations of the sampling sites are shown in Fig. 2, along with the estimated long-term mercury concentrations from AERMOD.

Mercury speciation was assessed by sequential selective extractions in two soil samples (locations H and I in Fig. 2) and two adobe brick samples (locations X and Z in Fig. 2). The selective extraction results (shown in Table 2) demonstrated that 90–97% and 91–93% of

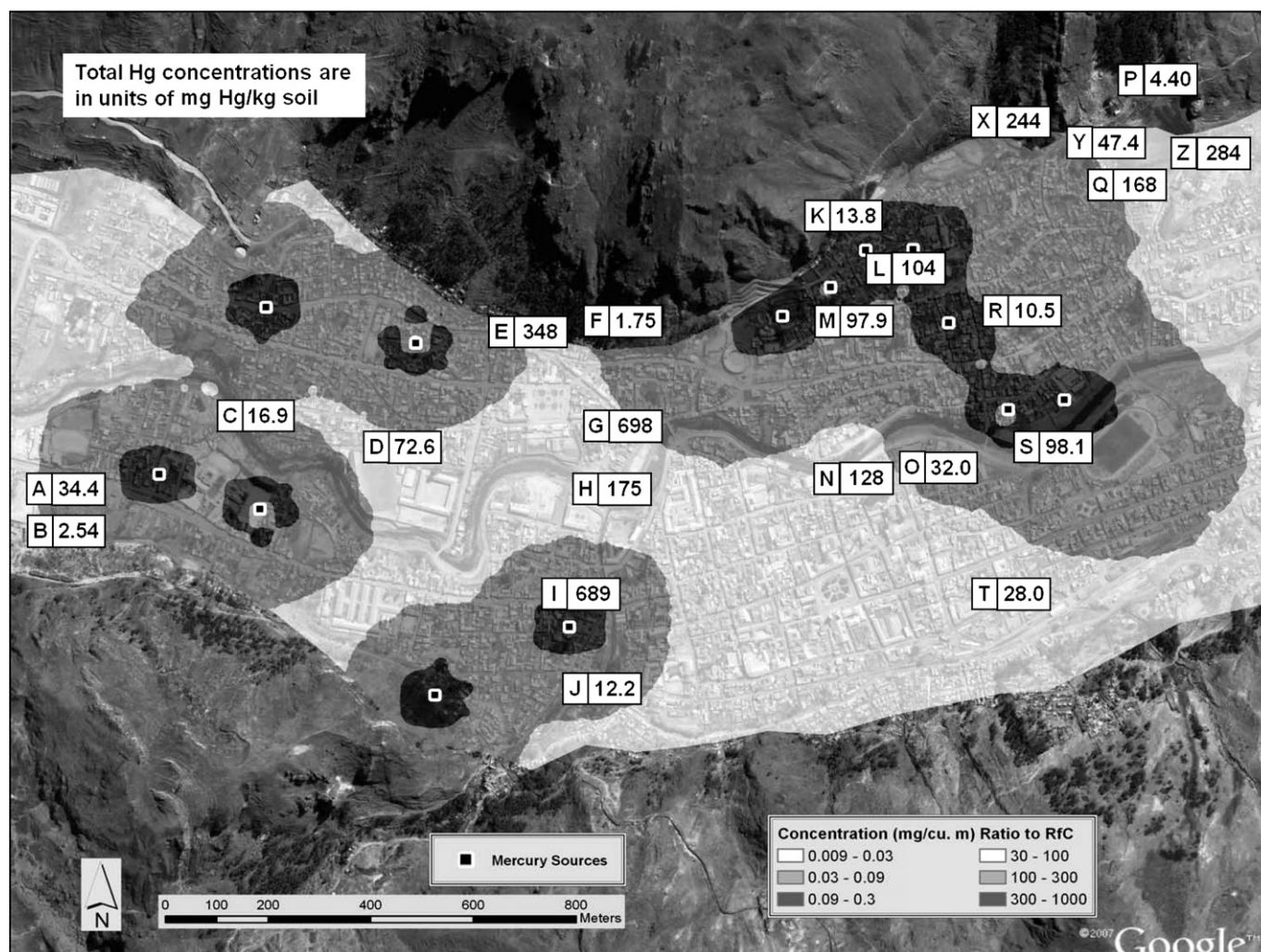


Fig. 2. Estimated long-term ambient air mercury concentrations for Huancavelica in 1680 and comparison with EPA Reference Concentration; sampling locations (letter indicates sampling site corresponding to data in Tables 2–4; number is average total mercury concentration).



**Table 2**

Selective extractions of Hg from two soil samples (H, I) and two adobe brick samples (X, Z).

mg/kg Hg leached in each reagent (% of total)					
Sampling site	Extraction 1: deionized water	Extraction 2: 0.2 M acetic acid (pH 2)	Extraction 3: 1 M KOH	Extraction 4: 12 M HNO <sub>3</sub>	Extraction 5: aqua regia (HCl + HNO <sub>3</sub> )
H	0.3 (0.1)	0.0 (0.0)	3.7 (1.5)	20 (8.1)	230 (90)
I	0.6 (0.0)	0.0 (0.0)	8.8 (0.6)	32 (2.0)	1600 (97)
X	0.3 (0.1)	0.1 (0.0)	3.9 (1.2)	15 (4.8)	300 (94)
Z	0.5 (0.1)	0.7 (0.2)	22 (5.2)	14 (3.2)	390 (91)

mercury in soil and adobe brick samples, respectively, were extracted in the final step (F5 aqua regia step) and a smaller amount extracted in the third and fourth steps (F3 KOH and F4 nitric acid steps), as shown in Table 2. These results suggest that a large proportion of the mercury in the soil and adobe brick samples are in sulfide mineral phases, such as cinnabar and metacinnabar, minerals that are chemically inert under most pH conditions and are soluble only with aqua regia (Bloom et al., 2003). The samples also contained approximately 1.5 to 6% organic carbon (Table 4); thus a smaller portion of the mercury could also be in the form of Hg bound to organic matter, which is expected to dissolve in the F3 step.

The selective extractions also resulted in 2% to 8% of the total leached in the F4 nitric acid step, which coincides with the step for elemental mercury (Bloom et al., 2003). The possible presence of elemental mercury in the soil was also supported by detectable quantities of gaseous elemental mercury (up to 2 µg/m<sup>3</sup>) during the 2010 sampling event (Table 3). These measurements were collected directly above the soil by a handheld sensor that is most sensitive to Hg<sup>0</sup>. For reference, the background ambient air concentration of Hg<sup>0</sup> in the Southern Hemisphere is around 0.0009 to 0.0012 µg/m<sup>3</sup> (Working Group on Mercury, 2001) gaseous Hg<sup>0</sup> and measurements above 0.5 µg/m<sup>3</sup> would be expected if there were a direct source of Hg<sup>0</sup> to the air.

**Table 3**

Total Hg content and soil characteristics for sample sites in Huancavelica, Peru. All samples were collected in June 2009, except for five samples (K, L, M, N, and O) that were collected in August 2010.

Sample site ID	Sample type	Total Hg in soil or adobe (mg/kg) <sup>a</sup>	Hg <sup>0</sup> vapor 1 m above soil (µg/m <sup>3</sup> ) <sup>b</sup>	pH <sup>c</sup>	%TC <sup>d</sup>	%IC <sup>e</sup>	%OC <sup>f</sup>
A	Soil	34.4 ± 4.65 (n = 3)	NA	4.56	6.90 ± 0.014 (n = 2)	0.02	6.88
B	Soil	2.54 ± 0.490 (n = 3)	NA	6.27	5.73	0.13	5.59
C	Soil	16.9 ± 16.9 (n = 3)	NA	7.21 ± 0.021 (n = 2)	6.99	4.95	2.04
D	Soil	72.6 ± 37.0 (n = 3)	NA	6.95	6.83	3.47	3.36
E	Soil	348 ± 60.8 (n = 3)	NA	7.19	1.71	0.23	1.48
F	Soil	1.75 ± 1.05 (n = 6)	NA	7.13	2.65 ± 0.001 (n = 2)	0.81	1.84
G	Soil	698 ± 451 (n = 3)	NA	6.97	2.82	0.16	2.66
H	Soil	175 ± 35.9 (n = 3)	NA	7.29	3.95 ± 0.017 (n = 2)	1.56	2.40
I	Soil	689 ± 23.3 (n = 3)	NA	7.14	8.07	3.83	0.74
J	Soil	12.2 ± 16.3 (n = 5)	NA	6.53	4.57 ± 0.058 (n = 2)	1.81	6.26
K	Soil	13.8 ± 2.74 (n = 3)	0.4 ± 0.5	7.45	7.25	5.13	2.12
L	Soil	104 ± 21.2 (n = 2)	0.5 ± 1.0	7.18	9.41 ± 0.880 (n = 2)	7.23	2.18
M	Soil	97.9 ± 11.3 (n = 3)	1.3 ± 0.4	7.39 ± 0.007 (n = 2)	8.63 ± 0.003 (n = 2)	7.30	1.33
N	Soil	128 ± 47.2 (n = 2)	1.0 ± 0.3	7.59	7.40	5.01	2.39
O	Soil	32.0 ± 17.3 (n = 2)	1.9 ± 0.4	6.97 ± 0.067 (n = 2)	3.72	1.88	1.84
P	Soil	4.40 ± 1.72 (n = 6)	NA	6.82	3.31	0.05	3.26
Q	Soil	168 ± 131 (n = 6)	NA	7.19	0.82	0.49	0.33
R	Soil	10.5 ± 2.21 (n = 3)	NA	7.45	12.2 ± 0.006 (n = 2)	10.7	1.51
S	Soil	98.1 ± 51.0 (n = 6)	NA	7.05	6.20	2.68	3.52
T	Soil	28.0 ± 10.8 (n = 6)	NA	6.97	3.15	0.31	2.84
X	Adobe	244 (n = 1)	NA	6.85 ± 0.014 (n = 2)	1.66	0.14	1.52
Y	Adobe	47.4 (n = 1)	NA	6.75	0.62 ± 0.011 (n = 2)	0.02	0.59
Z	Adobe	284 (n = 1)	NA	6.98	1.26	0.04	1.22

NA: data not available.

<sup>a</sup> Average (± 1 standard deviation) of total Hg samples in soil or adobe samples (n = number of replicate samples at each location).<sup>b</sup> Average (± 1 standard deviation) of 4 mercury vapor measurements taken about 1 m above the ground before soil samples were collected.<sup>c</sup> Average (± 1 standard deviation) of pH for measurements performed in duplicate (n = number of replicate measurements).<sup>d</sup> Percent total carbon; average (± 1 standard deviation) of %TC for measurements performed in duplicate (n = number of replicate measurements).<sup>e</sup> Percent inorganic carbon.<sup>f</sup> Percent organic carbon.**Table 4**

Soil texture.

Sample ID	Sample type	% clay (<2 µm)	% silt (2–50 µm)	% sand (>50 µm)
K	Soil	5.5	49.6	44.9
L	Soil	3.1	27.2	69.7
M	Soil	4.7	24.6	70.8
N	Soil	3.1	16.3	80.5
O	Soil	3.5	18.2	78.3
X, Y, Z (composite)	Adobe	6.0	20.8	73.2

Soil characteristics and texture are shown in Tables 3 and 4, respectively. The pH ranged between 4.56 and 7.59 (6.98 ± 0.63; average ± 1 SD) for soil samples and 6.75 and 6.98 (6.86 ± 0.12) for adobe brick samples. The total carbon in the soil samples was determined to be 5.69%TC ± 2.83, with organic carbon making up 2.69 ± 1.70% and inorganic carbon making up 3.00 ± 2.99%. Adobe brick samples contained 1.18 ± 0.53%OC, with organic carbon making up 1.11 ± 0.47% and inorganic carbon making up 0.07 ± 0.06%. The textures of the soil samples were 4.0 ± 1.1% clay, 27.2 ± 13.3% silt, and 68.8 ± 14.2% sand. The textures of the adobe brick composite sample were 6.0% clay, 20.8% silt, and 73.2% sand.

#### 4. Discussion

##### 4.1. Comparison of AERMOD concentration estimates to inhalation health effect reference values

To the best of our knowledge, this is the first study that compared estimated historical mercury ambient air concentrations with present-day inhalation reference values for elemental mercury vapor in order to estimate potential health risks from historical exposure to mercury refining in Huancavelica. The entire community of Huancavelica was

estimated to have been exposed to concentrations above the NIOSH Ceiling of 0.1 mg/m<sup>3</sup> for a 10-min duration, a value that should not be exceeded at any time. Areas closest to the mercury smelters were estimated to have experienced concentrations above 1.7 mg/m<sup>3</sup>, therefore exceeding the 1-h AEGL-2 value. Concentrations greater than the AEGL-2 can cause irreversible health effects; the AERGL-2 for elemental mercury was based on the potential to cause developmental effects and fetal toxicity.

The values used in this comparison range from 10-min to 1-h exposure durations and include values that are generally used in occupational and emergency response settings. In contrast, mercury smelters in Huancavelica were operating 24 h a day throughout most of the colonial period. The workers in the mercury smelters often lived near the mills, as did other members of the community, exacerbating exposures.

Estimates of maximum long-term mercury concentrations were extrapolated from the estimated 1-h maximum mercury concentrations. These values were compared with the EPA RfC of 0.0003 mg/m<sup>3</sup> for chronic exposure, which was based on clinical observations of neurological effects (e.g., hand tremor and memory disturbances) in exposed humans after application of a factor of 30 to account for susceptible individuals and for potential unknowns. The entire community of Huancavelica was estimated to have experienced levels of elemental mercury vapor that exceeded the RfC by a factor of 30 to 100. Areas within approximately 300 m of the mercury smelters exceeded the RfC by a factor of 100 to 300, while even closer to the sources the RfC was exceeded by a factor of 300 to 1000. Taken together, these historical populations were exposure to mercury at or above levels where effects were clinically observed in the population on which the RfC was based.

#### 4.2. Present-day soil measurements

Measured present-day soil concentrations in Huancavelica are shown in Fig. 2 on the map of estimated long-term historical atmospheric mercury concentrations. In a previous study using AERMOD to estimate historic atmospheric mercury concentrations in Potosí, Bolivia, present-day soil measurements demonstrated a concentration gradient

consistent with an air concentration gradient predicted by AERMOD (Hagan et al., 2011). In Huancavelica, the measured soil mercury concentrations did not clearly demonstrate the historic atmospheric mercury concentration gradient predicted by AERMOD, as was evident in the Potosí study. We attribute these patterns to differences in distribution of smelters throughout the city and differences in source characteristics used in the dispersion model in Huancavelica compared to Potosí. In Potosí, the sources were generally located in a straight line through the center of the city. Because of this location, one would expect the concentrations to be greater closer to the source and decrease with distance. In Huancavelica, the smelters were scattered in clusters throughout the city. Additionally, smelter characteristics in Huancavelica varied during the colonial period. Changes in stack heights from shorter stacks to taller stacks, along with relocation of the smelters, may also explain why higher concentrations of mercury in soil were measured in areas predicted by AERMOD to have lower historic atmospheric concentrations of mercury. Thus, while using AERMOD to estimate the present-day contamination from historic emissions of mercury can serve as a useful prediction tool in some communities (e.g., Potosí), in other communities, the situation may be more complicated and result in a more variable distribution of estimated air concentrations.

The present-day measured soil mercury concentrations in Huancavelica are similar to levels measured in soils at mercury mining sites and locations that use or have used mercury in a production process, as summarized in Table 5. In Almadén, Spain, the largest cinnabar mine in the world, concentrations of soil mercury in five studies range from 0.13 mg/kg at the lowest site to about 8900 mg/kg at the most contaminated site (Bernaus et al., 2005; Millán et al., 2006; Conde Bueno et al., 2009; Molina et al., 2006; Higuera et al., 2006). Idrija, Slovenia, the second largest cinnabar mine in the world, has residual concentrations of mercury in soil ranging from 0.385 mg/kg to nearly 2800 mg/kg (Kocman et al., 2004; Palinkaš et al., 1995; Gnamuš et al., 2000). The range of mercury in soil in Huancavelica is consistent with studies of the world's two largest mercury mines.

The concentrations of mercury in soil in Huancavelica are much greater than mercury measured in soil at locations that use or have historically

**Table 5**

Comparison of total mercury concentrations in soils from mercury mining districts, locations of mercury use, and background sites.

Location	No. of sampling locations	Range (total Hg, mg/kg)	Notes	Reference
<i>Mercury mining</i>				
Almadén, Spain	10	400–1820	Average of 3 replicates; No depth information provided	Bernaus et al., 2005
	10	5.03–1710	Average of 5 replicates from each location; Samples taken at a depth of 25 cm	Millán et al., 2006
	16	86.5–7315	Composite of 6 samples from each location; Samples taken at depths of 0–30 cm	Conde Bueno et al., 2009
	3	0.13–2695	Total number of samples: 53; Some sample analyses replicated; Samples taken at depths of 20–30 cm	Molina et al., 2006
Idrija, Slovenia	4	6–8889	Total number of samples: 67; No depth information provided	Higuera et al., 2006
	7	8.4–415	Composite of 5 samples from each core sample; Core samples taken 0–10 cm (5 samples), 0–1 m (2 samples)	Kocman et al., 2004
	56	0.4–87.6	Total of 100 samples taken: 52 single surface samples, 4 core samples (divided into 48 samples); No depth information provided	Palinkaš et al., 1995
Huancavelica, Peru	25	0.385–2759	Total of 182 samples taken; Samples taken at depths of 0–15 cm	Gnamuš et al., 2000
	15	1.75–698	Average of triplicate samples from each location; Samples taken at a depth of 2.5 and 7.5 cm	
<i>Mercury use</i>				
Guizhou, China	23	0.062–0.355	Composite of 3–5 samples; Samples taken at a depth of 10 cm	Li et al., 2008b
Potosí, Bolivia	15	0.105–155	Average of 6 replicates; Samples taken at depths of 2.5 and 7.5 cm	Hagan et al. 2011
Andacollo, Chile	6	2.5–47	Individual samples; Samples taken at depths of 15–25 cm	Higuera et al., 2004
Punitaqui, Chile	8	3.2–35	Individual samples; Samples taken at depths of 15–25 cm	Higuera et al., 2004
<i>Background</i>				
Uncontaminated soils		0.01–0.03	Detailed information of number of samples or sampling depth not provided	Senesil et al., 1999
Non-mining town in Bolivia (Sucre)	5	0.01–0.08	Average of duplicate samples from each location; Samples taken at depths of 2.5 cm and 7.5 cm	Hagan et al. 2011

used mercury in production processes. In Guizhou, China, mercury concentrations ranged from 0.062 mg/kg to 0.355 mg/kg, resulting from artisanal zinc smelting operations (Li et al., 2008b). Potosí, Bolivia was the site of historic silver refining using mercury amalgamation, and although amalgamation operations ceased in the early 1900s, present-day soil concentrations of mercury ranged from 0.105 mg/kg to 155 mg/kg (Hagan et al., 2011). In Andacollo and Panitauqui, Chile, where copper–gold–mercury mining occurs, mercury concentrations in soil ranged from 2.5 mg/kg to 47 mg/kg and 3.2 mg/kg to 35 mg/kg, respectively (Higueras et al., 2004).

The soil results indicate that the current population of Huancavelica is exposed to levels of total mercury that are among the highest in the world as a result of historical mercury contamination. If inhaled or ingested, the contaminated soil may present significant health effects to the residents of Huancavelica, depending on the type of the mercury present. Our analysis of the speciation of mercury in soil and adobe brick samples indicate that a large portion of this mercury was likely an inorganic mineral phase (e.g. cinnabar or metacinnabar) and a smaller portion in other phases (such as elemental mercury or mercury–organic matter complexes). As such, current residents are vulnerable to mercury exposure through inhalation or ingestion of mercury-bearing dust and possibly through inhalation of elemental mercury vapor (that volatilizes from their brick homes and soil). Children in Huancavelica are especially at risk from soil exposure. The median uptake by a 1-year-old toddler in the U.S. is estimated to be 100 mg of dirt and dust ingested per day, simply from hand-to-mouth activity (U.S. EPA, 2008). For this ingestion rate, the daily exposure for an 11 kg 1-year-old toddler (50th percentile body weight for U.S. males and females; U.S. EPA, 2008) would exceed EPA's Reference Dose (RfD) for inorganic mercury (0.3 mg/kg-day; U.S. EPA, 1995b) if the ingested soil and dust contained more than 33 mg/kg of soluble mercury. Total mercury concentrations exceeded 33 mg/kg in 55% of the soil samples and two of the adobe brick samples. It is important to consider that these ingestion rates and body weights are for U.S. children; children in Huancavelica and South America in general may have different ingestion rates and body weights. Not only do children have potentially higher levels of mercury exposure than adults, but also the likelihood and severity of adverse health effects are greater as well, as their brains and neurological systems are still developing (Evans, 1998).

## 5. Conclusions

The estimated ambient air concentrations of mercury suggest that there was widespread mercury contamination in Huancavelica during the colonial period when cinnabar mining and refining were occurring on a large-scale. The comparison of the dispersion model estimates with present-day inhalation reference values for elemental mercury vapor suggests that the entire community of Huancavelica was at risk of experiencing adverse health effects. Although the precise nature of health and neurological effects from mercury exposure was limited at the time, the historical record contains descriptions consistent with mercury poisoning (Robins, 2011; Robins and Hagan, 2012).

The estimated atmospheric concentrations of mercury from the colonial period were used to explore the extent to which the community currently residing in Huancavelica is exposed to mercury contamination from historical mining and refining operations. The AERMOD dispersion model estimates were used as a first approximation of the distribution of present-day concentrations of mercury in soil in Huancavelica. Average total mercury soil concentrations in Huancavelica ranged from 1.75 mg/kg to 698 mg/kg, 20 to 70,000 times greater than background soils in Sucre, Bolivia. These concentrations are among the highest mercury concentrations reported in surface soils, including in other locations of mercury mining and use. The estimated historical concentrations of mercury vapor will be used with the total mercury concentrations in present-day soil to guide a comprehensive evaluation of present-day mercury exposure, and associated health risks, in Huancavelica.

## Disclaimer

The information in this document has been funded in part by the U.S. Environmental Protection Agency. It has been subjected to review by the National Center for Environmental Assessment and approved for publication. The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency.

## Acknowledgments

Special thanks to Ted Palma, James Hirtz, James Thurman, and Roger Brode of the U.S. EPA for their support and contributions to this paper. Nicholas Robins additionally thanks Joseph Graff and Diego Ballivian of the Council for the International Exchange of Scholars Fulbright program, and Marcela Inch former Director of the National Archive and Library of Bolivia, and her staff, as well as Rubén Julio Ruiz Ortiz, Director of the Casa Nacional de Moneda, Potosí and Sheila Beltrán López, Director of the Museum of the Nacional de Moneda de Potosí, and Martin Crane Sr. and Jr. for their support of this research. Additionally, the authors would like to thank Richard Merrin, Miguel Yépez, and Carolina Avilés of the U.S. Embassy in Peru, for their assistance. Nicholas Robins and Nicole Hagan would jointly like to acknowledge support from Oak Ridge Institute of Science and Education fellowships at the U.S. EPA National Center for Environmental Assessment, Office of Research and Development. This research was supported by a grant from the Duke Global Health Institute.

## References

- ATSDR (Agency for Toxic Substances, Disease Registry). Toxicological profile for mercury. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service; 1999. Available: <http://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=115&tid=24> [accessed 10 January 2011].
- Bernaus A, Gaona X, Valiente M. Characterisation of Almadén mercury mine environment by XAS techniques. *J Environ Monit* 2005;7:771–7.
- Bloom NS, Preus E, Katon J, Hiltner M. Selective extractions to assess the biogeochemically relevant fractionation of inorganic mercury in sediments and soils. *Anal Chim Acta* 2003;479:233–48.
- Cooke CA, Blacom PH, Biester H, Wolfe AP. Over three millennia of mercury pollution in the Peruvian Andes. *Proc Natl Acad Sci* 2009;106:8830–4.
- Conde Bueno P, Bellido E, Martín Rubí JA, Jiménez Ballesta R. Concentration and spatial variability of mercury and other heavy metals in surface soil samples of periurban waste mine tailing along a transect in Almadén mining district (Spain). *Environ Geol* 2009;56:815–24.
- Evans H. Mercury. In: Rom W, editor. *Environmental and occupational medicine*. 3rd edition. New York: Lippincott-Raven Publishers; 1998. p. 1001.
- Gee GW, Or D. Particle-size analysis. In: Dane JH, Clarke Topp G, editors. *Methods of soil analysis, part 4—physical methods*. Wisconsin: Soil Science Society of America, Inc.; 2002. p. 255–94.
- Gnamuš A, Byrne AR, Horvat M. Mercury in the soil–plant–deer–predator food chain of a temperate forest in Slovenia. *Environ Sci Technol* 2000;34:3337–45.
- Hagan N, Robins N, Hsu-Kim H, Halabi S, Morris M, Woodall G, et al. Estimating historical atmospheric mercury concentrations from silver mining and their legacies in present-day surface soil in Potosí, Bolivia. *Atmos Environ* 2011;45:7619–26.
- Hendershot WH, Laland H, Duquette M. Soil reaction and exchangeable acidity. In: Carter MR, editor. *Soil sampling and methods of analyses*. Florida: Lewis Publishers; 1993. p. 141–6.
- Higueras P, Oyarzun R, Oyarzun J, Maturana H, Lillo J, Morata D. Environmental assessment of copper–gold–mercury mining in the Andacollo and Punitauqui districts, northern Chile. *Appl Geochem* 2004;19:1855–64.
- Higueras P, Oyarzun R, Lillo J, Sánchez-Hernández JC, Molina JA, Esbrí JM, et al. The Almadén district (Spain): anatomy of one of the world's largest Hg-contaminated sites. *Sci Total Environ* 2006;356:112–24.
- Kocman D, Horvat M, Kotnik J. Mercury fractionation in contaminated soils from the Idrija mercury mine region. *J Environ Monit* 2004;6:696–703.
- Li P, Feng X, Qiu G, Li Z, Fu X, Sakamoto M, et al. Mercury exposures and symptoms in smelting workers of artisanal mercury mines in Wuchuan, Guizhou, China. *Environ Res* 2008a;107:108–14.
- Li G, Feng X, Qiu G, Bi X, Li Z, Zhang C, et al. Environmental mercury contamination of an artisanal zinc smelting area in Weinan County, Guizhou, China. *Environ Pollut* 2008b;154:21–31.
- McGill WB, Figueiredo CT. Total nitrogen. In: Carter MR, editor. *Soil sampling and methods of analyses*. Florida: Lewis Publishers; 1993. p. 201–12.



- Millán R, Gamarra R, Schmid T, Sierra MJ, Quejido AJ, Sánchez DM, et al. Mercury content in vegetation and soils of the Almadén mining area (Spain). *Sci Total Environ* 2006;368:79–87.
- Molina JA, Oyarzun R, Esbrí J, Higuera P. Mercury accumulation in soils and plants in the Almadén mining district, Spain: one of the most contaminated sites on Earth. *Environ Geochem Health* 2006;28:487–98.
- NIOSH (National Institute for Occupational Safety and Health). NIOSH pocket guide to chemical hazards. Cincinnati, OH: National Institute for Occupational Safety and Health; 2006.
- NRC (National Research Council). Science and judgment in risk assessment. Washington, D.C.: National Academies Press; 1994.
- NRC (National Research Council). Standing operating procedures for developing acute exposure guideline levels (AEGs) for hazardous chemicals. Washington, D.C.: National Academies Press; 2001.
- OEHHA (Office of Environmental Health Hazard Assessment). Acute and chronic toxicity summary – mercury. Sacramento, CA: Office of Environmental Health Hazard Assessment, California EPA; 2008.
- Palinkaš L, Pirc S, Miko SF, Durn G, Namjesnik K, Kapelj S. The Idrija mercury mine, Slovenia, a semi-millennium of continuous operation: an ecological impact. In: Richardson M, editor. *Environmental toxicology assessment*. London: Taylor and Francis Ltd.; 1995.
- Revis NW, Osborne TR, Holdsworth G, Hadden C. Mercury in soil: a method for assessing acceptable limits. *Arch Environ Contam Toxicol* 1990;19:221–6.
- Robins N. Mercury, mining, and empire, the human and ecological costs of colonial silver mining in the Andes. Indiana: Indiana University Press; 2011.
- Robins N, Hagan N. Mercury production and use in colonial Andean silver production: emissions and health implications. *Environ Health Perspect* 2012. <http://dx.doi.org/10.1289/ehp.1104192>.
- Senesil GS, Baldassarre G, Senesi N, Radina B. Trace element inputs into soils by anthropogenic activities and implications for human health. *Chemosphere* 1999;39:343–77.
- Telmer K, Viegas MM. World emissions of mercury from artisanal and small scale gold refining. In: Pirrone N, Mason R, editors. *Mercury fate and transport in the global atmosphere: measurements, models and policy implications*. Interim Report of the UNEP Global Mercury Partnership on Mercury Air Transport and Fate Research; 2008.
- U.S. EPA (U.S. Environmental Protection Agency). Mercury, elemental. Available: <http://www.epa.gov/ncea/iris/subst/0370.htm>1995. [accessed 10 January 2011].
- U.S. EPA (U.S. Environmental Protection Agency). Mercuric chloride. Available: <http://www.epa.gov/ncea/iris/subst/0692.htm>1995. [accessed 10 January 2011].
- U.S. EPA (U.S. Environmental Protection Agency). Mercury Study Report to Congress. U.S. Environmental Protection Agency, Washington, DC, EPA-452/R-97-007. Available: <http://www.epa.gov/hg/report.htm>1997. [accessed 10 January 2011].
- U.S. EPA (U.S. Environmental Protection Agency). Method 7473 mercury in solids and solutions by thermal decomposition, amalgamation, and atomic absorption spectrophotometry. Available: <http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/7473.pdf>1998. [accessed 10 January 2011].
- U.S. EPA (U.S. Environmental Protection Agency). U.S. EPA Method 1631, Revision E: mercury in water by oxidation, purge and trap, cold vapor atomic fluorescence spectrometry. Available: [http://water.epa.gov/scitech/methods/cwa/metals/mercury/upload/2007\\_07\\_10\\_methods\\_method\\_mercury\\_1631.pdf](http://water.epa.gov/scitech/methods/cwa/metals/mercury/upload/2007_07_10_methods_method_mercury_1631.pdf)2002. [accessed 22 November 2011].
- U.S. EPA (U.S. Environmental Protection Agency). Child-Specific Exposure Factors Handbook (Final Report). U.S. Environmental Protection Agency, Washington, DC, EPA-600/R-06/096F. Available: <http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=199243#Download>2008. [accessed 10 January 2011].
- U.S. EPA (U.S. Environmental Protection Agency). Technology transfer network support center for regulatory atmospheric modeling: preferred/recommended models. Available: [http://www.epa.gov/scram001/dispersion\\_prefrec.htm#aermod](http://www.epa.gov/scram001/dispersion_prefrec.htm#aermod)2009. [accessed 10 January 2011].
- U.S. EPA (U.S. Environmental Protection Agency). Graphical arrays of chemical-specific health effect reference values for inhalation exposures (final report). U.S. Environmental Protection Agency, Washington, DC, EPA/600/R-09/061. Available: <http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=211003>2009. [accessed 10 January 2011].
- U.S. EPA (U.S. Environmental Protection Agency). Technology transfer network support center for regulatory atmospheric modeling: screening models. Available: [http://www.epa.gov/ttn/scram/dispersion\\_screening.htm#aerscreen](http://www.epa.gov/ttn/scram/dispersion_screening.htm#aerscreen)2010. [accessed 10 January 2011].
- Working Group on Mercury. Ambient air pollution by mercury (Hg): position paper. Luxembourg: Office for Official Publications of the European Communities; 2001. Available: <http://ec.europa.eu/environment/air/quality/background.htm> [accessed 22 November 2011].